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Relativistic Molecular Orbital Calculations for Polyatomic Molecules

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Relativistic molecular orbital calculations based on discrete variational Dirac-Fock-Slater method have been performed for the polyatomic molecules: CF_4 , SF_6 , UF_4 and UF_6 . For CF_4 and SF_6 molecules on which the relativity negligibly effects, identical results are obtained between the relativistic and nonrelativistic calculations. Result of UF_6 is equivalent to the data in the previous papers. That for UF_4 is in much better agreement with experimental ionization energies than the values presented in the other work.

KEY WORDS: Relativistic molecular orbital calculation/Discrete variational Dirac-Fock-Slater method/Discrete variational $X\alpha$ method/ UF_6 / UF_4 /

I. INTRODUCTION

Electrons in molecules have high velocity near the nuclei of heavy atoms such as Au, Pb, U, comparable to the light. Electronic structures for the molecules containing those heavy atoms should be estimated with the relativistic wave equation. There are lots of methods to evaluate the relativistic effects in atoms and molecules.^{1,2)} The relativistic effects are, however, too large for the heavy atoms to be dealt by perturbation of nonrelativistic wavefunctions. They increase abruptly with the atomic number. This extent can be indicated by velocity ratio of 1s electrons to the light³⁾ and by spin-orbit energies which are comparable with bond energies for the molecules with the heavy atoms.⁴⁾ Discrete variational Dirac-Fock-Slater (DV-DFS) method is based on fully relativistic scheme and one of powerful techniques.⁵⁾

In the present paper, we ensure the validity for one of DV-DFS computation programs first. Electronic structures obtained by the relativistic calculations are checked up with those by the nonrelativistic calculations for the CF_4 and SF_6 molecules where the relativistic effects are negligibly small. When the effects are studied through comparison between the relativistic and the nonrelativistic results, it is valuable to confirm the exact accordance of the relativistic and the nonrelativistic results for the molecules made up of light elements. For the CO and

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UO diatomic molecules, the present program has been checked already.⁶⁾ Using a final version of program passing in the checks for the CF₄ and SF₆ molecules, we obtain electronic structures for UF₄ and UF₆ and compare them with experimental data.

II. COMPUTATIONAL METHOD

The computational details of nonrelativistic DV-X α method used in the present work have been described elsewhere.⁷⁾ Nonrelativistic one-electron Hamiltonian is :

$$H = p^2 + V(r), \quad (1)$$

where the first term represents the kinetic energy, the second term the potential energy and $p = -i\hbar\nabla$ is the momentum operator. In the Slater's X α approximation, the exchange part V_x in the potential is described with local electron density ρ as follows :

$$V(r) = V_{en}(r) + V_c(r) + V_x(r), \quad (2)$$

$$V_x(r) = -3\alpha \left\{ \frac{3}{8\pi} \rho(r) \right\}^{1/3}, \quad (3)$$

where V_{en} and V_c are the potential operators due to electron-nucleus interactions and Coulomb interactions among the electrons.

In the Dirac-Fock-Slater method, relativistic one-electron Hamiltonian is :

$$H = c\hat{\alpha} \cdot p + \beta mc^2 + V(r), \quad (4)$$

where c is the velocity of light and m is the rest mass of electron. The operators $\hat{\alpha}$ and $\hat{\beta}$ are the Dirac matrices :

$$\hat{\alpha} = \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix}, \quad (5)$$

$$\hat{\beta} = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}, \quad (6)$$

where σ is the 2×2 Pauli spin matrix and I is the 2×2 unit matrix. The averaged density of up- and down-spins are used for V_x which is expressed by the same equation as eq.(3) in the present work. The molecular wavefunctions are expanded by symmetry-adapted orbitals ϕ :

$$\phi(r) = \sum_{\nu, m} w_{km; \nu} \varphi_{nkm}(r_\nu), \quad (7)$$

The coefficient w is obtained by means of the projection operator in the group theory. The φ is a wavefunction for a spherical atom and expressed by

$$\varphi_{nkm}(r) = \frac{1}{r} \begin{pmatrix} P_{n\kappa}(r) \chi_{\kappa m}(\vartheta, \phi) \\ iQ_{n\kappa}(r) \chi_{-\kappa m}(\vartheta, \phi) \end{pmatrix}. \quad (8)$$

Table I. Summary of used parameters (atomic units) of molecular geometries, wells for SSO and sampling points.

	CF ₄	SF ₆	UF ₄	UF ₆
Symmetry	<i>Td</i>	<i>Oh</i>	<i>Td</i>	<i>Oh</i>
Distances *	2.500	2.955	3.892	3.778
Radii of well	7	7	10	8
Depth of well	-1	-1	-1	-1
α	0.7	0.7	0.7	0.7
Number of Sampling points	3000	6000	7000	6000

* Distances between the central atom and the fluorine atom.

Here P and Q are radial parts and the two-component function χ consists of spherical harmonics, spin functions and Clebsh-Gordan coefficients.

A summary of parameters used in the present work is shown in Table I. The parameters of wells added on the single site orbitals (SSO)^{8,9)} were chosen so that the generated atomic orbitals formed an efficient basis set. The well radii more than 7au resulted in the equivalent eigenvalues. Smaller radii in this range were suitable for efficient numerical integration. The self-consistent charge procedure was used to approximate the self-consistent field.¹⁰⁾

III. RESULTS AND DISCUSSION

To check the validity for the DV-DFS program, we compare two results which are derived by the relativistic and the nonrelativistic methods. For the CF₄ molecule, the relativistic effects are negligible because of small nuclear charges of the constituent atoms. Orbital populations and atomic effective charges are shown in Table II. Identical results are obtained by the relativistic and the nonrelativistic methods. Energy eigenvalues and orbital components are shown in Table III and IV for the nonrelativistic and the relativistic cases, respectively. They agree quite well with each other within the precision of DV integration.

Data concerning electron distribution and eigenvalues for the SF₆ molecule are likewise shown in Table V, VI and VII. The results by the nonrelativistic and the relativistic methods are consistent with each other. Relativistic effects cause differences in the inner-shell levels, especially the $1a_{1g}$ and $1\gamma_{6u}$ levels, where the electron densities are high near the sulfur nucleus.

Next, the electronic structures for the UF₆ and the UF₄ molecules are obtained by the DV-DFS method. They are compared with the results of the previous theoretical and the experimental works. Eigenvalues for the UF₆ molecule are shown in Table VIII. The present calculation reproduced the essentially same results as those of the previous DV-DFS calculations.^{11,12)} Some differences in Ref. 11 from the other data may come from omitting interaction between the inner-shell and the valence orbitals. It has been reported that the energies of valence levels obtained in the previous works are in good agreement with experimental ionization energies. Discussion on bonding characters for the UF₆ molecule will

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Table II. Orbital Populations for CF₄ molecule.

Elements	AO	Populations	
		Relativistic	Nonrelativistic
C	1s	2.02	2.02
	2s	1.02	1.01
	2p _{1/2}	0.72	2.15
	2p _{3/2}	1.43	
	3s	0.22	0.23
	3p _{1/2}	0.08	0.23
	3p _{3/2}	0.16	
Effective charges		0.37	0.37
F	1s	2.00	2.00
	2s	1.70	1.70
	2p _{1/2}	1.76	5.27
	2p _{3/2}	3.51	
	3s	0.09	0.09
	3p _{1/2}	0.01	0.02
	3p _{3/2}	0.02	
Effective charges		-0.09	-0.09

Table III. Nonrelativistic energy eigenvalues and orbital components for CF₄.

MO	Eigenvalues (eV)	Orbital components (%)									
		F					C				
		1s	2s	2p	3s	3p	1s	2s	2p	3s	3p
1t ₂	-659.37	100									
1a ₁	-659.37	100									
2a ₁	-278.53						101				
3a ₁	-36.76		66	9	-6	-6		34		3	
2t ₂	-33.41		78	3	4	5			11		-1
4a ₁	-19.52		26	51	-2	1		16		8	
3t ₂	-17.65		5	64	5				25		
1e	-13.70			100							
4t ₂	-13.06			97	-1	-1					5
1t ₁	-12.05*			101		-1					
5a ₁	-1.23		1	1	169	4		-4		-72	
5t ₂	-0.10			1	21	111					-33
6t ₂	0.99			5	9	86			10		-9
2e	1.13					100					
6a ₁	1.72		3	9	-2	82		1		7	

* Highest occupied molecular orbital.

Table IV. Relativistic energy eigenvalues and orbital components for CF₄.

MO	Eigenvalues (eV) **	Orbital components (%)											
		F						C					
		2s	2p _{1/2}	2p _{3/2}	3s	3p _{1/2}	3p _{3/2}	2s	2p _{1/2}	2p _{3/2}	3s	3p _{1/2}	3p _{3/2}
1 γ_8	-660.05												
1 γ_7	-660.05												
1 γ_6	-660.05												
2 γ_6	-278.56												
3 γ_6	-36.76	66	3	6	-7	-2	-4	35			3		
2 γ_8	-33.43	78	1	1	5		5			11		-1	
2 γ_7	-33.42												
4 γ_6	-19.51	26	17	34	-2		1	16			8		
3 γ_8	-17.60	5	33	32	5		1			25			
3 γ_7	-17.58												
4 γ_8	-13.67		34	67									
4 γ_7	-13.04		97		-1	-1						5	
5 γ_8	-12.98			97	-1		-1						5
5 γ_6	-12.04		67	34									
6 γ_8	-12.01*		16	84									
6 γ_6	-1.23	1	1	1	169	1	3	-4			-72		
7 γ_8	-0.10			1	20		115						-37
5 γ_7	-0.10			1	18	117						-36	
8 γ_8	1.00		3	3	8	38	48			10			-9
6 γ_7	1.01			5	8	10	77		10			-9	
9 γ_8	1.14					33	67						
7 γ_6	1.72	3	3	6	-2	27	54	1			7		

* Highest occupied molecular orbital.

** Pairs correspond with nonrelativistic degenerate levels.

Table V. Orbital Populations for SF₆ molecule.

Elements	AO	Populations	
		Relativistic	Nonrelativistic
S	1s	2.00	2.00
	2s	2.02	2.02
	2p _{1/2}	2.00	6.00
	2p _{3/2}	4.00	
	3s	0.07	0.10
	3p _{1/2}	0.89	2.65
	3p _{3/2}	1.77	
	3d _{3/2}	0.82	2.05
	3d _{5/2}	1.23	
	4s	0.91	0.81

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	$4p_{1/2}$	0.14	0.49
	$4p_{3/2}$	0.29	
Effective charges		-0.13	-0.13
F	1s	2.00	2.00
	2s	1.83	1.91
	$2p_{1/2}$	1.70	5.13
	$2p_{3/2}$	3.39	
	3s	0.05	0.00
	$3p_{1/2}$	0.00	-0.06
	$3p_{3/2}$	0.00	
Effective charges		0.02	0.02

Table VI. Nonrelativistic energy eigenvalues and orbital components for SF₆.

MO	Eigenvalues (eV)	Orbital components (%)				
		S		F		
		3p	3d	2s	2p	3s
1a _{1g}	-2408.62					
1t _{1u}	-658.95					
1e _g	-658.95					
2a _{1g}	-658.94					
3a _{1g}	-223.90					- 1
2t _{1u}	-171.04					
4a _{1g}	-38.55			61	13	20
3t _{1u}	-34.28	17		76	5	
2e _g	-32.46		16	106	6	-21
5a _{1g}	-22.39			37	27	-11
4t _{1u}	-18.55	27		11	53	4
1t _{2g}	-15.45		21		79	
3e _g	-14.46		5	- 3	93	6
5t _{1u}	-12.63				96	2
1t _{2u}	-12.47				100	
1t _{1g}	-11.40*				100	
6a _{1g}	-5.10			1	58	25
6t _{1u}	-0.85	54			35	47
7a _{1g}	-0.54				2	98
7t _{1u}	0.25	9			5	-53

* Highest occupied molecular orbital.

Table VII. Relativistic energy eigenvalues and orbital components for SF₆.

MO	Eigenvalues (eV)**	Oobital components (%)							
		S				F			
		3p _{1/2}	3p _{3/2}	3d _{3/2}	3d _{5/2}	2s	2p _{1/2}	2p _{3/2}	3s
1γ _{6g}	-2417.88								
1γ _{8g}	-661.48								
2γ _{6g}	-661.48								
1γ _{8u}	-661.48								
1γ _{6u}	-661.48								
3γ _{6g}	-226.31								
2γ _{6u}	-173.02								
2γ _{8u}	-171.74								
4γ _{6g}	-40.26					60	4	9	21
3γ _{6u}	-35.96	17				74		6	1
3γ _{8u}	-35.95		17			74	3	3	1
2γ _{8g}	-34.13			6	9	96	1	2	-11
5γ _{6g}	-23.90					36	9	17	-13
4γ _{6u}	-20.00	28				14	1	51	3
4γ _{8u}	-19.99		27			14	26	27	3
3γ _{8g}	-16.95			12	9		41	38	
1γ _{7g}	-16.94				21			80	
4γ _{8g}	-15.92			3	3	- 1	29	61	6
5γ _{6u}	-14.11						93	3	2
5γ _{8u}	-14.05						5	91	1
6γ _{8u}	-13.89						52	49	
1γ _{7u}	-13.86							100	
6γ _{6g}	-12.88						67	33	
5γ _{8g}	-12.85*						17	84	
7γ _{6g}	-6.64					1	20	41	20
6γ _{6u}	-2.31	59				1	1	40	19
7γ _{8u}	-2.22		60			1	19	20	22
8γ _{6g}	-0.97						1	1	96
7γ _{6u}	-0.11	3						2	-14
8γ _{8u}	-0.11		3				1	1	-20

* Highest occupied molecular orbital.

** Pairs correspond with nonrelativistic degenerate levels.

appear elsewhere.¹³⁾

Table IX summarizes orbital populations for the UF₄ molecule. There are large differences in the uranium 5f and 6d populations between the nonrelativistic and the relativistic results. Owing to small electron densities near the nucleus, these orbitals are expanded by the relativistic contraction of inner-shell orbitals and their populations change considerably.

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Table VIII. Comparison of eigenvalues for UF₆.

Eigenvalues (eV)			
MO	PW*	Ellis**	Kim***
9 γ_{8g}	-12.31	-12.47	-14.0
10 γ_{8g}	-12.03	-11.82	-13.7
4 γ_{7g}	-11.96	-11.73	-13.4
9 γ_{6u}	-11.65	-11.59	-13.2
10 γ_{8u}	-11.64	-11.60	-13.2
9 γ_{6g}	-11.23	-11.06	-13.6
3 γ_{7u}	-11.17	-11.10	-12.8
11 γ_{8u}	-11.17	-11.10	-12.9
10 γ_{6u}	-10.41	-10.27	-12.2
10 γ_{6g}	-10.17	-10.28	-12.2
11 γ_{8g}	-10.14	-10.25	-12.2
12 γ_{8u}	- 9.28	- 9.19	-11.0
4 γ_{7u}	- 6.72	- 6.89	- 7.9
13 γ_{8u}	- 5.61	- 5.89	
5 γ_{7u}	- 5.52	- 5.76	
14 γ_{8u}	- 4.10	- 4.38	
11 γ_{6u}	- 4.07	- 4.20	

* Present work.

** Ref. 12.

***Ref. 11.

Eigenvalues are shown in Table X, together with those reported previously.¹⁴⁾ There are large discrepancies between Ref. 14 and the present work. Experimental ionization energies are also shown.¹⁵⁾ Although calculations by the transition state method are necessary to get the ionization energies in the Slater's approximation, it is possible to compare the energies in the ground state with the experimental ones, because the transition state calculations give almost uniformly lower-shifted energies in narrow energy ranges such as valence electrons for most molecules. As uniform shifts about -4eV were found in the data of Ref. 14, the levels were shifted by -4.15eV instead of the transition state calculations in the present work. It is notable to examine the valence levels (12 γ_7 -19 γ_8) whose main component is the fluorine 2p. The width of levels in the present work agrees well with the experimental, while that in Ref. 14 is two times larger.

To confirm the valence structure in the present work, the relativistic levels are correlated with the nonrelativistic ones in Fig. 1. The variations from the nonrelativistic valence levels to the relativistic can be essentially explained in terms of spin-orbit splitting and uniform shifts due to change of electron distribution caused by indirect relativistic effects.³⁾ Orbital components are shown in Table XI. In the fluorine 2p valence levels, the uranium 6p and 7p components contribute to the large splitting of 19 γ_8 -13 γ_7 pair. The other levels are shifted almost uniformly upward. The fluorine atomic orbitals are hardly affected by the relativity, if they are alone. The shifts can be interpreted as a result of the expansion of uranium valence

Table IX. Orbital Populations for UF₄ molecule.

Elements	AO	Populations	
		Relativistic	Nonrelativistic
U	1s	2.00	2.00
	2s	2.00	2.00
	2p _{1/2}	2.00	6.00
	2p _{3/2}	4.00	
	3s	2.00	2.00
	3p _{1/2}	2.00	6.00
	3p _{3/2}	4.00	
	3d _{3/2}	4.00	10.00
	3d _{5/2}	6.00	
	4s	2.00	2.00
	4p _{1/2}	2.00	6.00
	4p _{3/2}	4.00	
	4d _{3/2}	4.00	10.00
	4d _{5/2}	6.00	
	4f _{5/2}	6.00	14.00
	4f _{7/2}	8.00	
	5s	2.00	2.00
	5p _{1/2}	2.00	6.00
	5p _{3/2}	4.00	
	5d _{3/2}	4.00	10.0
	5d _{5/2}	6.00	
	5f _{5/2}	2.32	3.84
	5f _{7/2}	0.79	
	6s	1.98	1.95
	6p _{1/2}	1.97	5.78
	6p _{3/2}	3.84	
	6d _{3/2}	0.63	1.14
	6d _{5/2}	0.75	
	7s	0.10	0.05
	7p _{1/2}	0.12	0.18
	7p _{3/2}	0.19	
	7d _{3/2}	0.10	0.19
	7d _{5/2}	0.14	
Effective charges		1.06	0.85
F	1s	2.00	2.00
	2s	1.90	1.91
	2p _{1/2}	1.78	5.24
	2p _{3/2}	3.53	
	3s	0.03	0.02
	3p _{1/2}	0.01	0.05
	3p _{3/2}	0.03	
Effective charges		-0.27	-0.21

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Table X. Comparison of ionization energies for UF₄.

Energies (eV)						
Present work			Experimental**	Ellis***		
MO	GS*	Shifted*		MO	GS*	TS*
9 γ_6	-49.79			1 γ_6	-45.8	-50.2
10 γ_7	-33.41			3 γ_8	-30.1	-34.2
14 γ_8	-30.12			2 γ_7	-30.1	-34.1
10 γ_6	-28.95			2 γ_6	-27.4	-31.2
11 γ_7	-27.96			3 γ_7	-25.8	-29.8
15 γ_8	-22.43			4 γ_8	-21.4	-25.6
12 γ_7	-11.33	-15.48	-16.13	5 γ_8	-12.4	-16.1
16 γ_8	-11.32	-15.47		3 γ_6	-10.4	-14.1
11 γ_6	-11.20	-15.35	-15.58	6 γ_8	-10.2	-13.9
17 γ_8	-11.09	-15.24		4 γ_7	-9.1	-13.5
12 γ_6	-10.67	-14.82	-14.72	4 γ_6	-9.1	-12.8
18 γ_8	-10.63	-14.78		5 γ_7	-9.0	-12.7
13 γ_7	-10.09	-14.24	-13.94	7 γ_8	-8.8	-12.5
19 γ_8	-9.47	-13.62	-13.62	8 γ_8	-6.9	-10.7
20 γ_8	-5.78	-9.93	-10.32	9 γ_8	-2.6	-6.8

- * GS: Ground state,
Shifted: GS values were shifted by -4.15eV,
TS: Transition state.
** Ref. 15.
***Ref. 14.

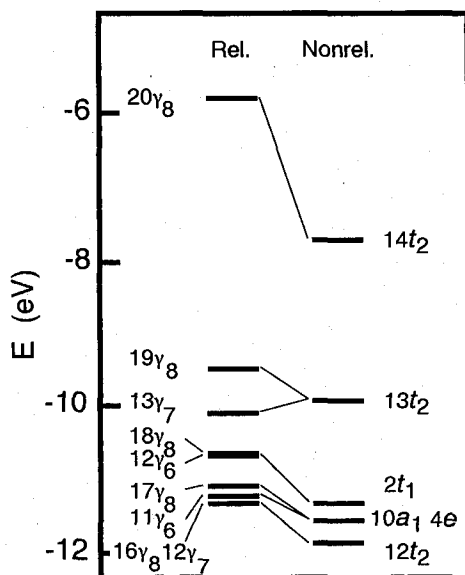


Fig. 1. Correlation between relativistic and nonrelativistic valence levels for UF₄.

Table XI. Relativistic energy eigenvalues and orbital components for UF₄.

Eigenvalues		Orbital components (%)												
		U										F		
MO	(eV)**	5f _{3/2}	5f _{5/2}	6s	6p _{1/2}	6p _{3/2}	6d _{3/2}	6d _{5/2}	7s	7p _{1/2}	7p _{3/2}	2s	2p _{1/2}	2p _{3/2}
9γ ₆	-49.79			98								1		1
10γ ₇	-33.41				79					- 1		17		2
14γ ₈	-30.12					15	1	1			- 1	76	1	1
10γ ₆	-28.95	1	1	1					4			94		1
11γ ₇	-27.96				19			3		2		76		
15γ ₈	-22.43					76	1	1			3	17	2	2
12γ ₇	-11.33	}	4					7		1		2	78	5
16γ ₈	-11.32		3	1		1	8	2			2	2		80
11γ ₆	-11.20	5	5						1			3	28	57
17γ ₈	-11.09						4	10					30	55
12γ ₆	-10.67	}	8	5									59	28
18γ ₈	-10.63		5	8									14	73
13γ ₇	-10.09	}			1					3			6	90
19γ ₈	- 9.47					4						1	44	48
20γ ₈	- 5.78*	85	5				3	2						4
13γ ₆	- 5.56	72	4						18					9
14γ ₇	- 5.07		92					6					1	
14γ ₆	- 4.78	8	72						12				9	1
21γ ₈	- 4.66	5	84				1						2	9
22γ ₈	- 1.34						40	36			1		4	12
15γ ₆	- 1.21	3	8						11			1	1	1
15γ ₇	- 0.94		1					22		51			7	
23γ ₈	- 0.53						5	10			43			5
16γ ₇	0.26		1					17		- 4			2	
24γ ₈	0.32						11	13			- 4			3

* Highest occupied molecular orbital.

** Pairs correspond with nonrelativistic degenerate levels.

orbitals which induces more negative electrostatic field on the fluorine atoms. One feature of the induced redistribution of electrons is observed in the increase of fluorine effective charge in Table IX. The relativistic results consistent with the nonrelativistic ones.

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